Observing the synthesis of a polymer brush, molecule by molecule

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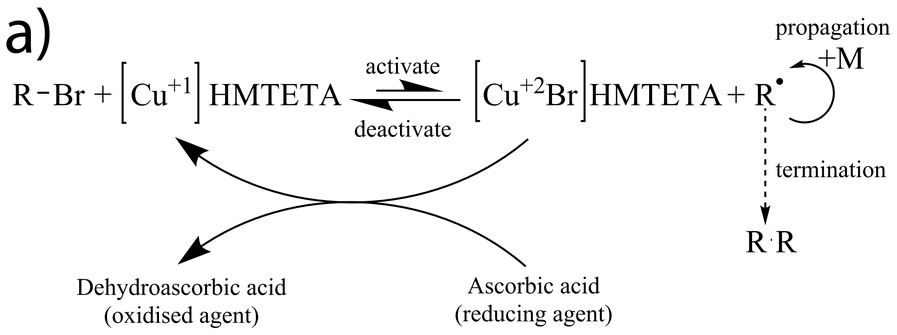
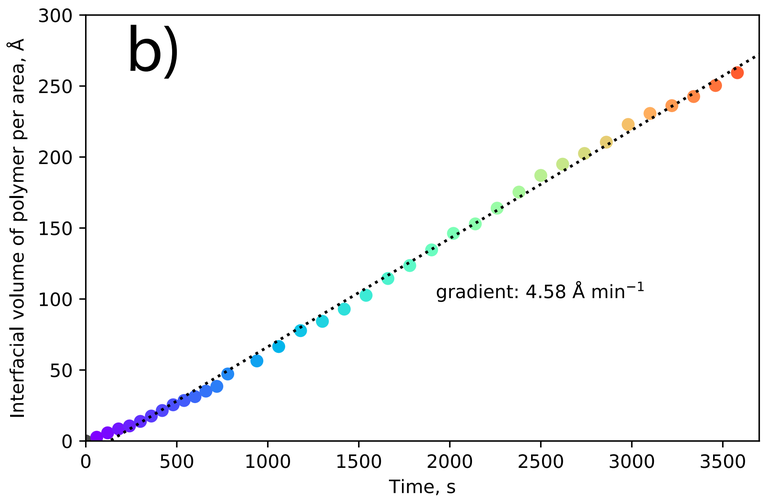
Introduction

Surface tethered polymer chains imbue coated surfaces with antifouling and lubricating properties. To produce these 'polymer brushes' with desirable molecular weights and grafting densities polymers must be grown from surface anchored initiators. ARGET ATRP (fig. a) is a common scheme for conducting this grafting-from polymerisation; however, the implications of polymerising from anchored initiators is not known. The crowded environment[2] and high catalyst to initiator ratio[1,3] are thought to produce a dense, cross-linked layer adjacent to the substrate, observable via neutron reflectometry[4] (fig. b).

This work aims to determine the origin and composition of this proximal layer.

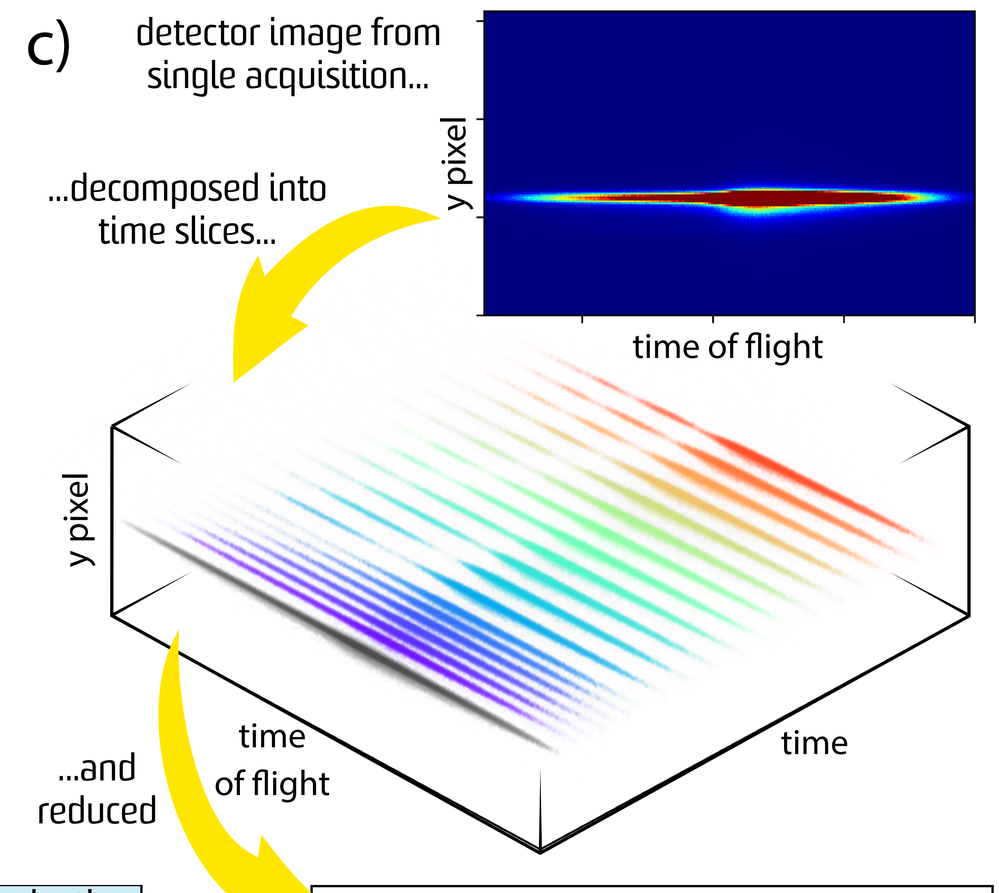
a)

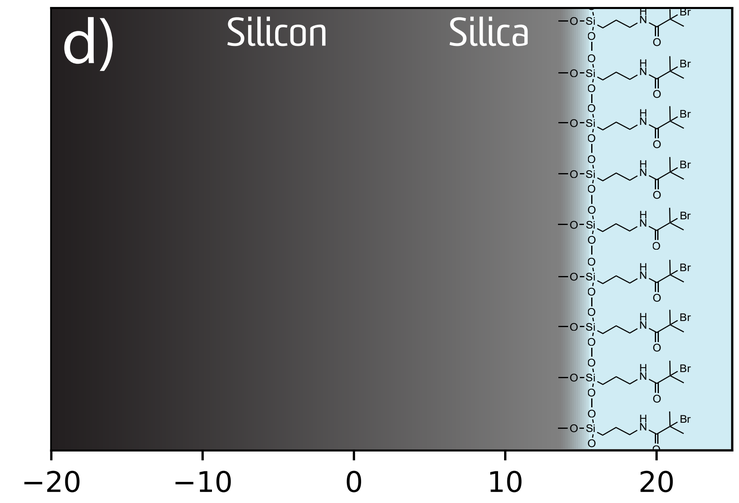


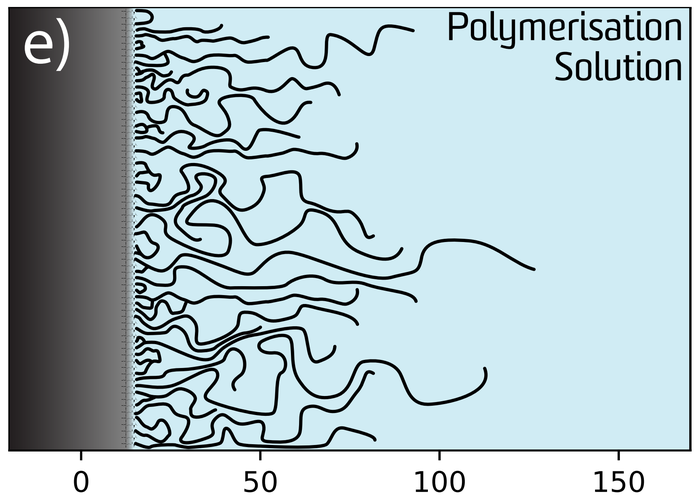


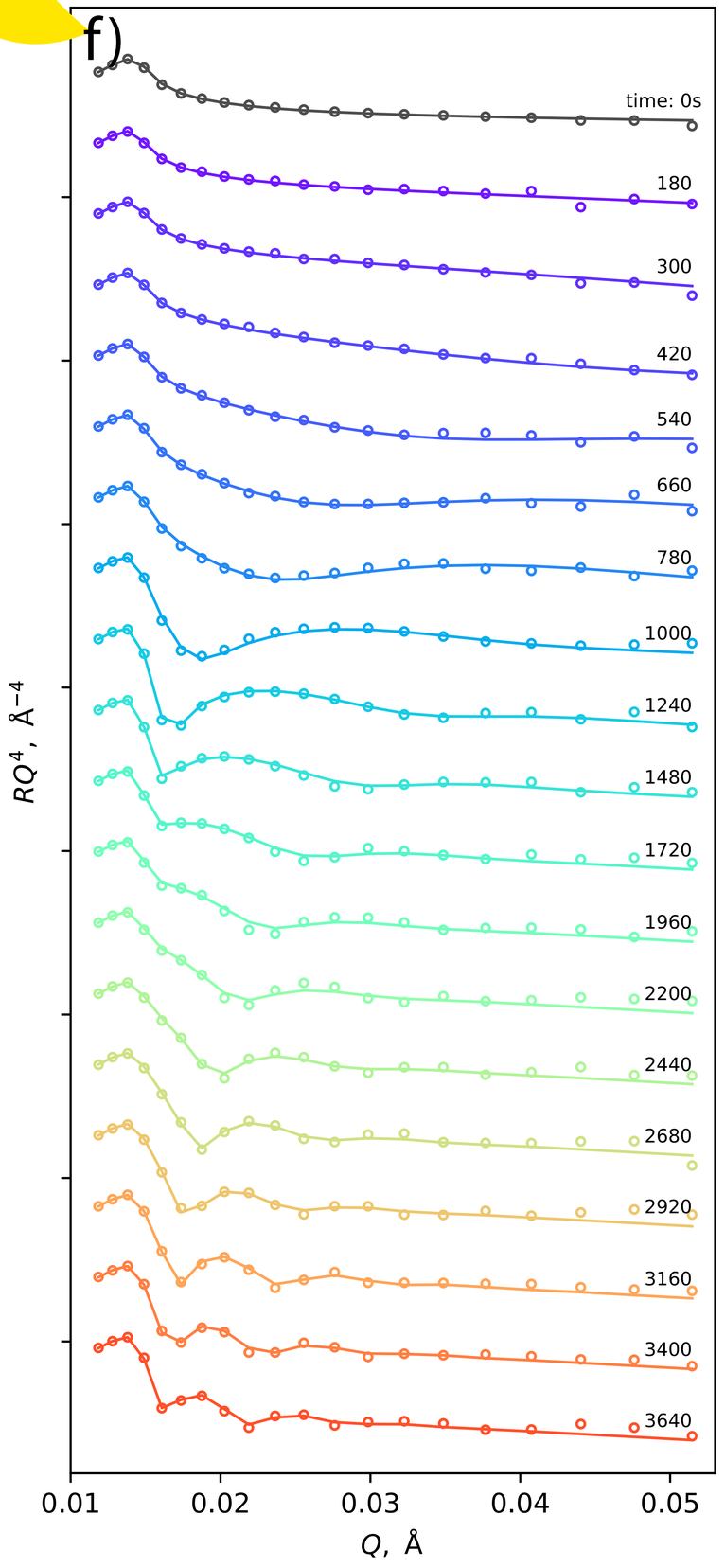
Experiment

The Platypus reflectometer was used to observe the synthesis of a poly(*N*-isopropylacrylamide) (PNIPAM) brush via ARGET ATRP. Polymerisation initiators were tethered to a silicon wafer (fig. d) and the polymerisation carried out in a standard solid-liquid cell using deuterated solvents to maximise contrast. Event-mode reduction in refnx[5] (fig. c) was used to produce time-dependent reflectometry profiles (fig. f).



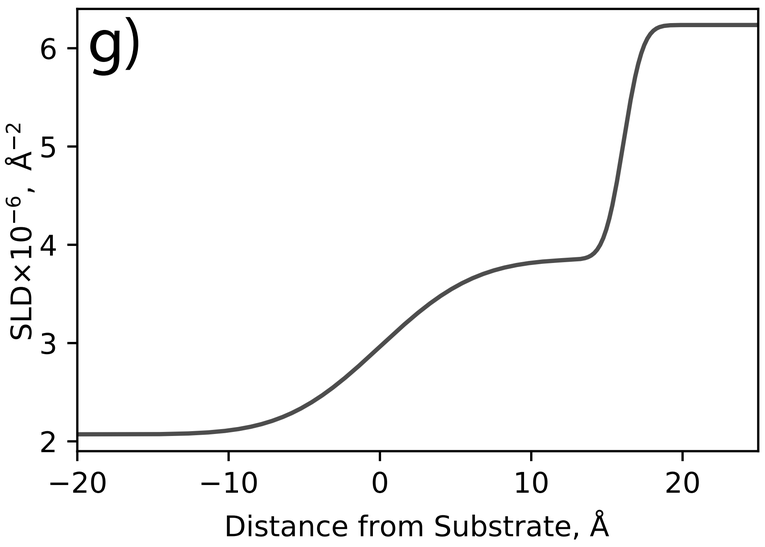


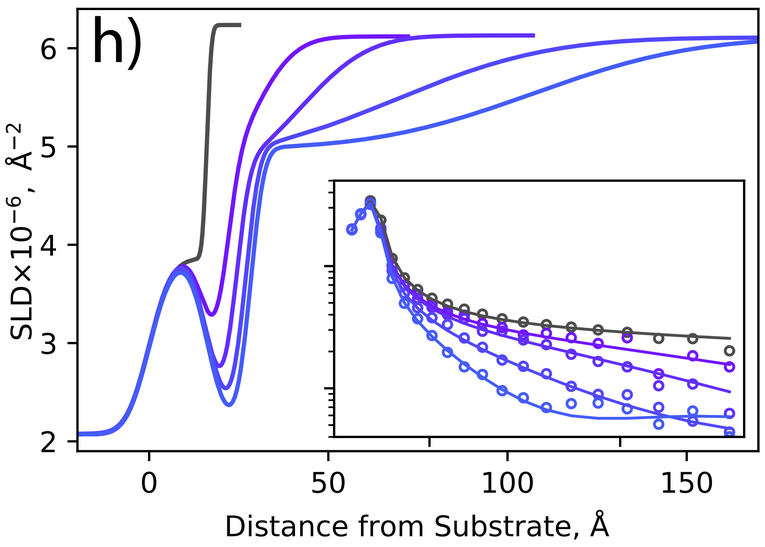


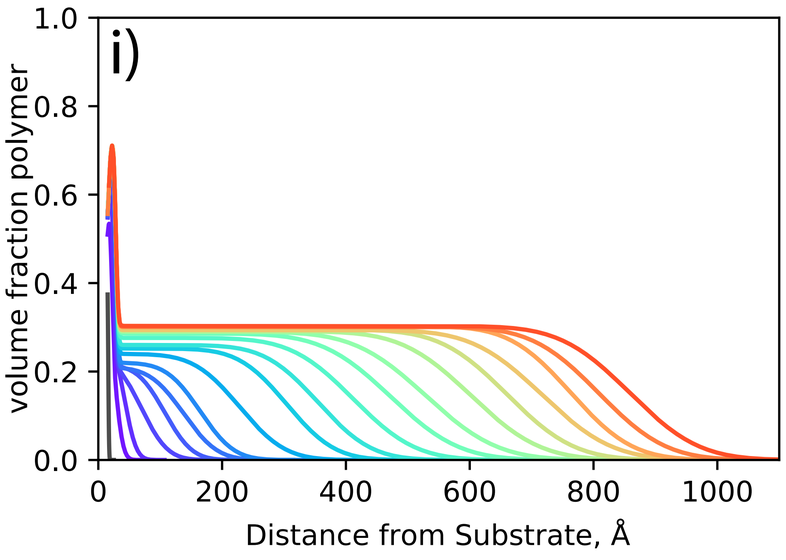


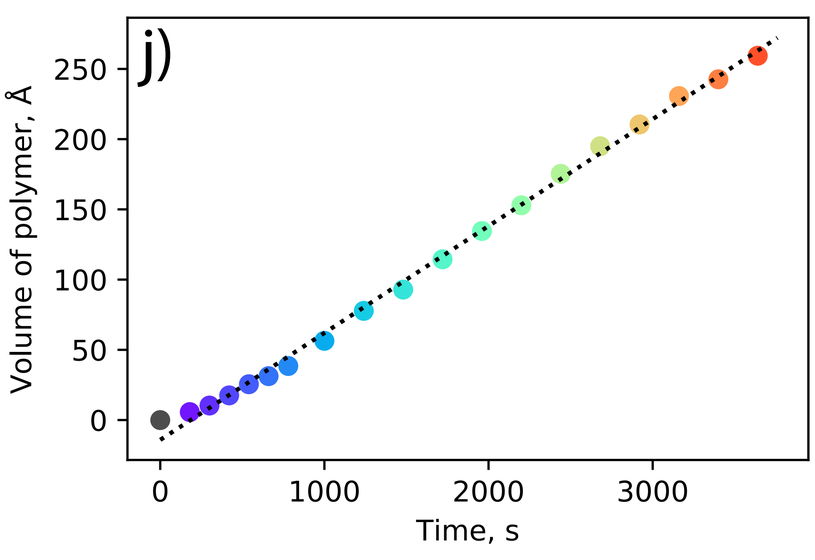
Results and Conclusion

The proximal layer was not observed pre-synthesis (fig. d, g), rather appearing early in the polymerisation (fig. e, h). Therefore, it can be concluded that the layer is composed of stunted polymer chains, rather than a thick initiator layer. The progression of the polymerisation was also observed (fig. i) and found to be linear (fig. j) after the formation of the proximal layer.









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